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In-situ hydrothermal synthesis of three-dimensional MnO_2–CNT nanocomposites and their electrochemical properties

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ABSTRACT

Three-dimensional (3-D) MnO_2–carbon nanotube (CNT) nanocomposites were prepared by a simple one-pot hydrothermal method. An electrode was then prepared with these nanocomposites. For comparative investigation, MnO_2 microspheres were also hydrothermally prepared without adding CNTs. The as-synthesized MnO_2 microspheres were then mechanically mixed with CNTs to prepare a subsequent electrode. The samples were characterized by electron microscopy, X-ray diffraction, and electrochemical methods. It has been revealed that a 3-D conductive network of CNTs was formed with microspheres of MnO_2 nanorods interwoven with and connected by CNTs. As a result, the hydrothermally mixed MnO_2–CNT electrode showed a higher specific capacitance than the mechanically mixed electrode. It has therefore been concluded that the hydrothermal mixing method yields a more homogeneous product that is better suited to take full advantages of both the high capacitance of MnO_2 and the high electrical conductivity of CNTs. The 3-D MnO_2–CNT nanocomposites reported herein have provided a promising electrode material for supercapacitors and other electrochemical energy storage/conversion devices.

1. Introduction

Recently, supercapacitors [1] have attracted intensive research interest due to their capability to deliver very high power density, which makes them indispensable candidates as power boosters for hybrid electric vehicles, mobile electronic devices, distributed sensor networks, and so on. The chemical energy of a supercapacitor is stored in the electrical double-layer (EDL) between the electrode and the electrolyte [2]. The fast, non-Faradayic discharge of the EDL enables supercapacitors to deliver very high power density. Moreover, the energy density or capacitance of an electrochemical supercapacitor can be significantly improved by introducing pseudocapacity. MnO_2 is among the most promising pseudocapacitor electrode materials due to its large specific capacitance, environmentally benign nature, and cost effectiveness [3–7]. Nevertheless, a major drawback of MnO_2 is its poor electrical conductivity, which limits its power-delivery capability. An effective approach to overcome this disadvantage is the introduction of electronically conductive materials, such as graphite [8], carbon nanofibers [9] and CNTs [3,10–29]. Among them, CNTs have been intensively investigated for their excellent conductivity, large intrinsic area, and chemical stability. CNTs are also reported to form well-controlled microstructures with MnO_2 for supercapacitor applications, such as MnO_2 nanowires on CNT paper [30], coaxial MnO_2–CNT arrays [31], and MnO_2 nanoflowers on vertically aligned CNT arrays [32]. It has been demonstrated that the electrochemical performances of electrodes can be significantly improved by employing MnO_2–CNT composite structures. In these composite structures, the large interfacial area between MnO_2 and electrolyte can enhance the electrochemical utilization of MnO_2 in the nanocomposites. The increased contact area between MnO_2 and CNTs, as well as their intimate bonding, is also desirable for the improvement of the electrical conductivity of the nanocomposite electrode due to the intrinsic high conductivity of CNTs [33,34]. It has been reported that the nanocomposite microstructure has an important influence on their electrochemical properties. To ensure optimal electrochemical performance, it is very important to obtain MnO_2 nanoparticles uniformly distributed on a conductive network of CNTs. The contact resistance between MnO_2 and CNTs should also be minimized by intimately bonding them together. Such characteristics in the microstructures of MnO_2–CNT nanocomposites obviously take root in the methods that are employed to prepare them, which can be classified into physical/mechanical-mixing [35,36] and chemical/electrochemical deposition [19–25]. It is therefore desirable to effectively synthesize nanocomposites with the above-mentioned optimal structural characteristics with a simple method.

In this work, a novel 3-D MnO_2–CNT nanocomposite was prepared by a simple one-pot hydrothermal method. The process resulted in a highly porous structure of a conductive CNT network

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uniformly filled and interwoven with highly dispersed, hierarchical microspheres consisting of MnO_2 nanorods. The CNTs and MnO_2 nanorods can be intimately bonded to each other, so as to render the following distinct characteristics to the 3-D MnO_2–CNT nanocomposites: (i) the improved electrical conductivity due to the presence of the CNT conductive network; (ii) the enhanced electrochemical accessibility of electrolyte due to the porous electrode structure. Such a homogeneous, hybrid microstructure can take advantage of the excellent intrinsic properties of both MnO_2 and CNTs. The samples were characterized by field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), X-ray energy dispersive spectroscopy (EDX) and X-ray diffractometry (XRD). The capacitive behaviors of the 3-D MnO_2–CNT nanocomposite electrode were investigated and compared to those of a mechanically mixed composite electrode. The comparative study was also carried out to reveal the impact of preparation methods on the microstructures and electrochemical properties of nanocomposite electrodes.

2. Experimental

2.1. Chemicals

The deionized water used in this work was prepared in house with a Thermo Scientific D4521 B-pure deionization system. All other chemicals were of analytical grade and used as received. Multi-wall carbon nanotubes (CNTs) were purchased from MER Corporation. $MnSO_4{\cdot}H_2O$, $(NH_4)_2S_2O_8$, Na_2SO_4, polytetrafluoroethylene (PTFE) and *N*-methyl-2-pyrrolidone were purchased from Sigma–Aldrich.

2.2. Preparation of the samples

The 3-D MnO_2–CNT nanocomposites were prepared by an *in-situ* hydrothermal method. Specifically, 0.025 g of CNTs was added to a 35 mL aqueous solution containing 0.02 g of $MnSO_4{\cdot}H_2O$ and 0.026 g of $(NH_4)_2S_2O_8$. The mixture was stirred for 2 h to form a stable suspension, and then loaded into a Teflon®-lined stainless-steel autoclave (capacity: 50 mL). The autoclave was heated to 90 °C and kept at this temperature for 24 h. The autoclave was then naturally cooled to room temperature. The black precipitate was separated by centrifugation, and then washed with water and ethanol three times. After that, the recovered product was dried at 80 °C in a vacuum oven for 24 h. The weight percentage of CNTs in the MnO_2–CNT sample is calculated to be 5 wt%. For comparison, γ-MnO_2 microspheres were prepared by a similar procedure without adding CNTs.

2.3. Characterization

Scanning electron microscopy (SEM) images were taken by using a Hitachi S-4700 field-emission scanning electron microscopy (FE-SEM). The FE-SEM samples were coated with a 5-nm thin layer of platinum/chromium using DC sputtering. The acceleration voltage was 15 keV and the acceleration current was 1.2 nA. The morphology, structure, and composition of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-4000FX) equipped with electron diffraction energy dispersive X-ray spectroscopy (EDX) at an acceleration voltage of 200 kV. The powders were ultrasonically dispersed in ethanol, and then deposited on a thin amorphous carbon film supported by a copper grid. The crystal structures of the samples were characterized by X-ray powder diffractometer (XRD, Rigaku D/MAX-RB), using graphite monochromatized Cu K_α radiation (λ = 0.154 nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 10–70° (2θ) at a scanning rate of 5° min^{-1}.

2.4. Electrode fabrication and electrochemical characterization

The fabrication processes of the electrodes are described as follows: the hydrothermally synthesized MnO_2–CNT powder (95 wt%) was mixed with PTFE (5 wt%) in an agate mortar. The mixture was then ground sufficiently to ensure good homogeneity, wherein *N*-methyl-2-pyrrolidone was used as solvent. The resultant slurry was cast onto the pre-cleaned stainless-steel plate. The electrode was air-dried overnight and then dried at 80 °C in a vacuum oven for 24 h. The as-prepared electrode was designated as HE. The loading was determined by a weighing method. For comparison, γ-MnO_2 nanorod microspheres (95 wt%) were mechanically mixed with CNTs (5 wt%) in an agate mortar, and the mixture was then ground sufficiently to ensure homogeneity. Finally, this mixture (95 wt%) was mixed with PTFE (5 wt%), wherein *N*-methyl-2-pyrrolidone was used as solvent. The electrode was prepared with the same procedures as mentioned above and designated as ME.

Cyclic voltammetry and galvanostatic charge–discharge measurements were performed using a potentiostat/galvanostat (Princeton Applied Research P/G, V4) with a three-electrode configuration. Pt wire and Ag/AgCl (saturated KCl, 0.222 V vs. standard hydrogen electrode) were employed as the counter and reference electrodes, respectively. Prior to testing, 0.5 M Na_2SO_4 solutions were purged with N_2 for 0.5 h and then used as the electrolyte. Cyclic voltammetry was performed in the potential range of 0.1–0.8 V at different scanning rates. The chronopotential test was performed in the potential range of 0–1 V at a current density of 1 mA cm^{-2}.

3. Results and discussion

3.1. Microstructures and crystal structures of the samples

Fig. 1 shows the FE-SEM micrographs of the as-synthesized samples. Fig. 1a demonstrates the uniform microspheres with an average size of about 5 μm, observed in the as-synthesized MnO_2 sample without adding CNTs. At a higher magnification (Fig. 1b), these microspheres show hierarchical structures consisting of nanorods with a diameter of about 30 nm and a length of about 1 μm. The as-synthesized MnO_2–CNT nanocomposites are shown in Fig. 1c–e. Observed from Fig. 1c, the sample is composed of 5-μm MnO_2 microspheres that are connected together by CNTs. At a higher magnification (Fig. 1d), it can be observed that some MnO_2 nanorods have been directly deposited on the surface of the CNTs. It is also noticed that the microspheres are evenly distributed in the network of CNTs. The hierarchical structure of a microsphere is again observed with CNTs interwoven within them (Fig. 1e). It is hypothesized that the negative MnO_4^- ions could be adsorbed onto the positively charged CNT surface by electrostatic attraction [37]. Under hydrothermal conditions, the redox reaction between Mn^{2+} and MnO_4^- may take place on the CNT surface [25,28]. Therefore, MnO_2 can grow on the CNT surface and eventually lead to the interweaving 3-D structure of CNTs and microspheres. The highly porous 3-D structure with nanotube/nanowire components can shorten the diffusion path for charge-carrier ions, while the large liquid–solid interface facilitates ion exchange between the electrode and electrolyte. Moreover, the uniformly embedded electronic conducting network can improve the high-rate capability as well as the specific capacitance of the materials [38].

The MnO_2–CNT nanocomposites are also characterized by HRTEM. Fig. 2a shows the formation of MnO_2 nanorods in the MnO_2–CNT nanocomposites. The ED patterns in Fig. 2b reveal the single-crystalline nature of the MnO_2 nanorods. Fig. 2c shows a typical ED pattern of CNTs. The lattice fringe with a *d*-spacing of 0.34 nm in Fig. 2d corresponds to the (1 1 1) plane of CNTs. The element compositions of the sample are also inspected by EDX, with results shown in Fig. 2f. It is noted that the peaks of copper are caused by the copper grid, which is used as a holder.

The samples were further characterized by XRD. Fig. 3a shows the XRD patterns of the CNTs, the diffraction peak at a 2θ value of 26° was ascribed to the typical (0 0 2) reflection of CNTs [11,39,40]. Fig. 3b shows the XRD patterns of the 3-D MnO_2–CNT nanocomposites. In addition to a very weak (0 0 2) diffraction peak of CNTs, all the other peaks can be indexed to the γ-MnO_2 (JCPDS no. 14-0644), indicating the formation of γ-MnO_2–CNT nanocomposites. Fig. 3c shows the XRD patterns of the sample prepared without adding CNTs, confirming the formation of pure γ-MnO_2 crystals.

3.2. Electrochemical properties of the electrodes

Fig. 4a shows the typical cyclic voltammograms (CVs) of the HE electrode at different scanning rates in a potential range of 0.1–0.8 V. The nearly rectangular shape of the CVs verifies the characteristics of a nearly ideal supercapacitor. It can also be observed that the current density gradually increases with the scanning rate. This indicates that the electrolyte ions can sufficiently contact the active electrode materials. It is well known that the power characteristics of an electrode material strongly depend on the electrochemical kinetics of the redox reaction. Since the capaci-